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Surfactant-Enhanced Luminescence Lifetime for Biomolecular Detection on Luminescent Gold Surfaces Decorated with Transition Metal Complexes

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Abstract

In the development of sensors based on multimodal detection, luminescent probes are attractive for providing a sensitive signal read-out, based either on intensity, wavelength shift or luminescence lifetime. The implicit simplicity of the devices that can be created is dependent of the judicious design of the multimodal probe. We have used transition metal probes which offer combined versatility due to their electroactive and photoluminescent properties, as well as their sensitivity to local environment. We report the influence of surfactant upon the formation of luminescent surfaces with metal complexes based on ruthenium(II) , iridium(III) and osmium(II) bearing surface active groups. The results reveal an enhancement of the luminescence lifetime when a mixed monolayer with surfactant is formed. Characteristically, the luminescence lifetime of the ruthenium tris-bipyridyl complex attached to the gold surface increases from 210 ns to 765 ns in the presence of a fluorinated surfactant. The luminescence signal of the modified gold surfaces is also responsive to bovine serum albumin and fetal bovine serum adsorption, demonstrating interaction of the protein

with the metal complex in the presence of the surfactant. The biomolecular interaction with the functionalised surfaces is also evidenced by surface plasmon resonance response.

Introduction

Optical and electrochemical detection of analytes are popular methods for a broad range of sensing applications due to their versatility and applicability for bench-top devices.[1] A key role for signal detection is the choice of probe with a reliable, sensitive response to the analyte. [2] Transition metal probes are photo- and electro- active with good stabilities. Their luminescence properties are particularly attractive as they offer three modes of signal detection through spectral wavelength, luminescence lifetime and luminescence intensity. The formation of monolayers of coordination complexes on planar surfaces has attracted interest in recent years and are generally characterised by lower surface concentrations than their organic counterparts.[3] The density of the layers can influence the interactions of analytes with the surface[4] or the orientation of the active surface probes.[5] In the detection of biomolecular analytes, the interactions of the analyte with the surface may interfere with signal detection. We have previously introduced transition metal complexes with long tethers MbpySS M = Ru, Ir, Os for attachment to gold. The complexes formed luminescent monolayers on gold surfaces[6] as the long tethers positioned the luminescent probe further away from the gold surface which has been shown to quench luminescence emission of transition metal complexes.[7] It was also reported that the ruthenium and iridium metal complexes could be assembled in a controlled manner through micropatterning techniques, forming red and green luminescent patterns upon stamping the surface.[6] In this study, we examine the effect of surfactant on the formation of the monolayers and its influence on protein binding.

Coating of nanomaterials by surfactants plays an important role on the growth of nanostructures or controlled aggregation of nanoparticles.[8] Most recently, the presence of surfactants has shown improved enzyme immobilisation.[9]

We have examined the luminescence properties of RubpySS and IrbpySS and OsbpySS[6, 8b] monolayers in the presence of fluorinated surfactants and the subsequent adsorption of the well-studied protein Bovine Serum Albumin (BSA) and the more biologically relevant Fetal Bovine Serum (FBS) (Figure 1).[10] Fluorinated surfactants have been previously shown to prevent aggregation of gold nanoparticles coated with metal complexes and have shown to lead to increase of the luminescence lifetime of the metal complex.[8b, 11] We have compared the properties with polyethylene glycol, which is commonly used in nanoparticle formulation for their interactions with biological media.

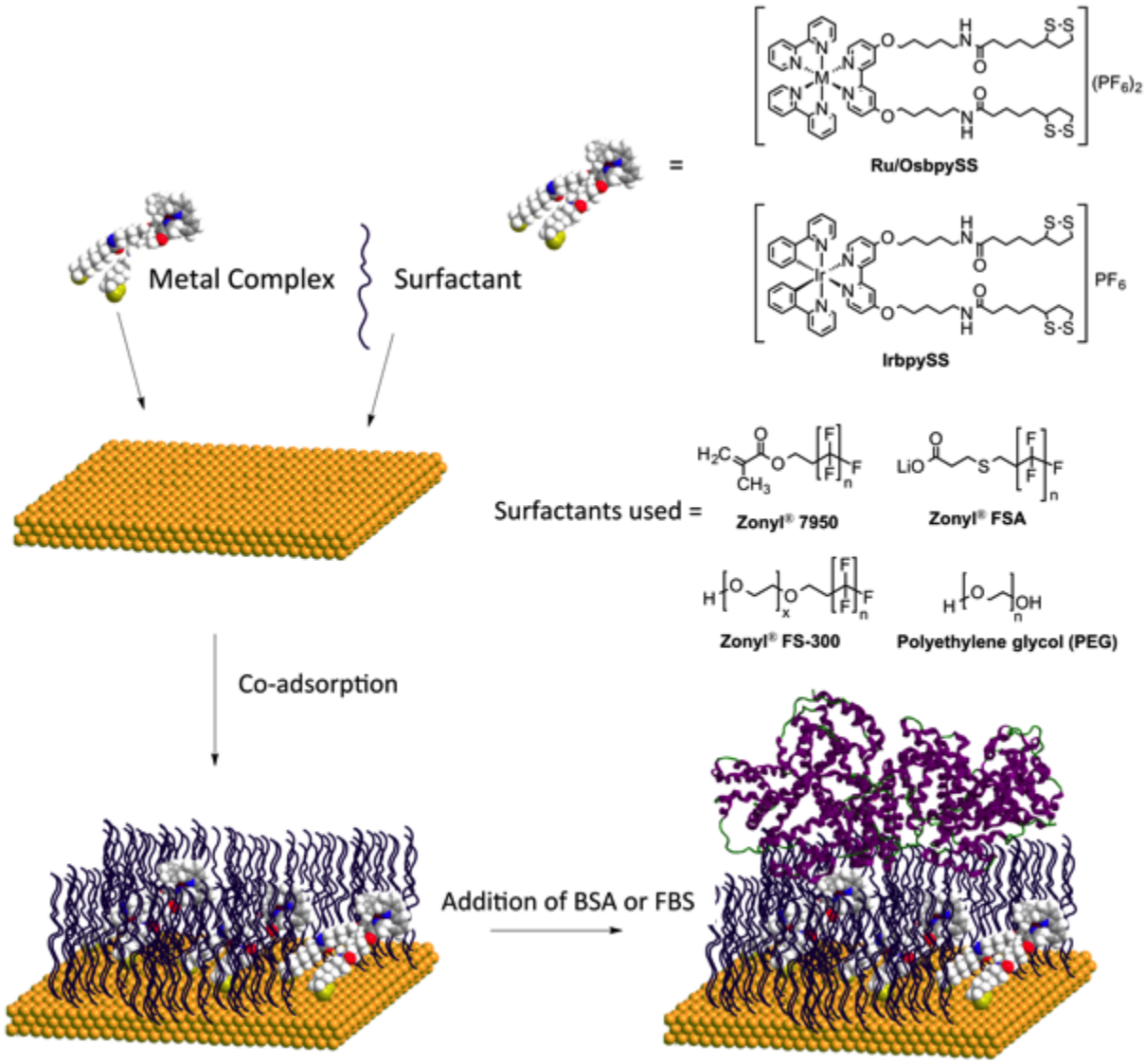

Figure 1. Schematic diagram of attachment of complexes and surfactants to gold surface and subsequent addition of BSA or FBS.

Results and Discussion

Luminescence Studies

The luminescence intensity and lifetime of the mixed monolayer systems on gold were examined to show the effect of surfactant on the properties of the luminescent probe and its effect on addition of protein. The properties of the fluorinated surfactants (Zonyl® 7950, Zonyl® FSA, Zonyl® FS-300) were compared with polyethylene glycol (PEG). A cleaned gold substrate was immersed in a 1 mM aerated acetonitrile solution of RubpySS or IrbpySS containing *ca.* 50 µL of surfactant for 24 hours. Following this, the substrates were washed in acetonitrile and examined by steady state and time-resolved luminescence spectroscopy. Excitation of the modified surfaces was targeted at the charge transfer band of the complexes and the emission is monitored from the triplet charge transfer. Monolayer samples of RubpySS•Au and IrbpySS•Au display the characteristic charge transfer based emission at 630 nm and 532 nm respectively. Addition of the surfactant to RubpySS surfaces causes little or no shift in the emission maxima apart from the case of Zonyl® 7950, which leads to a 20 nm blue shift (Figure 2, Table 1). A blue shift is also observed for the surfaces of IrbpySS, co-coated with Zonyl® 7950 which is in contrast with the 30 nm red shift observed for IrbpySS:PEG·Au (Figure 3, Table 2). The bare gold surface did not show any luminescence signal under the experimental conditions used but some strong scattering peaks notable in Figure 2c at 720 nm and in Figure 3 at 475 could not be eliminated.

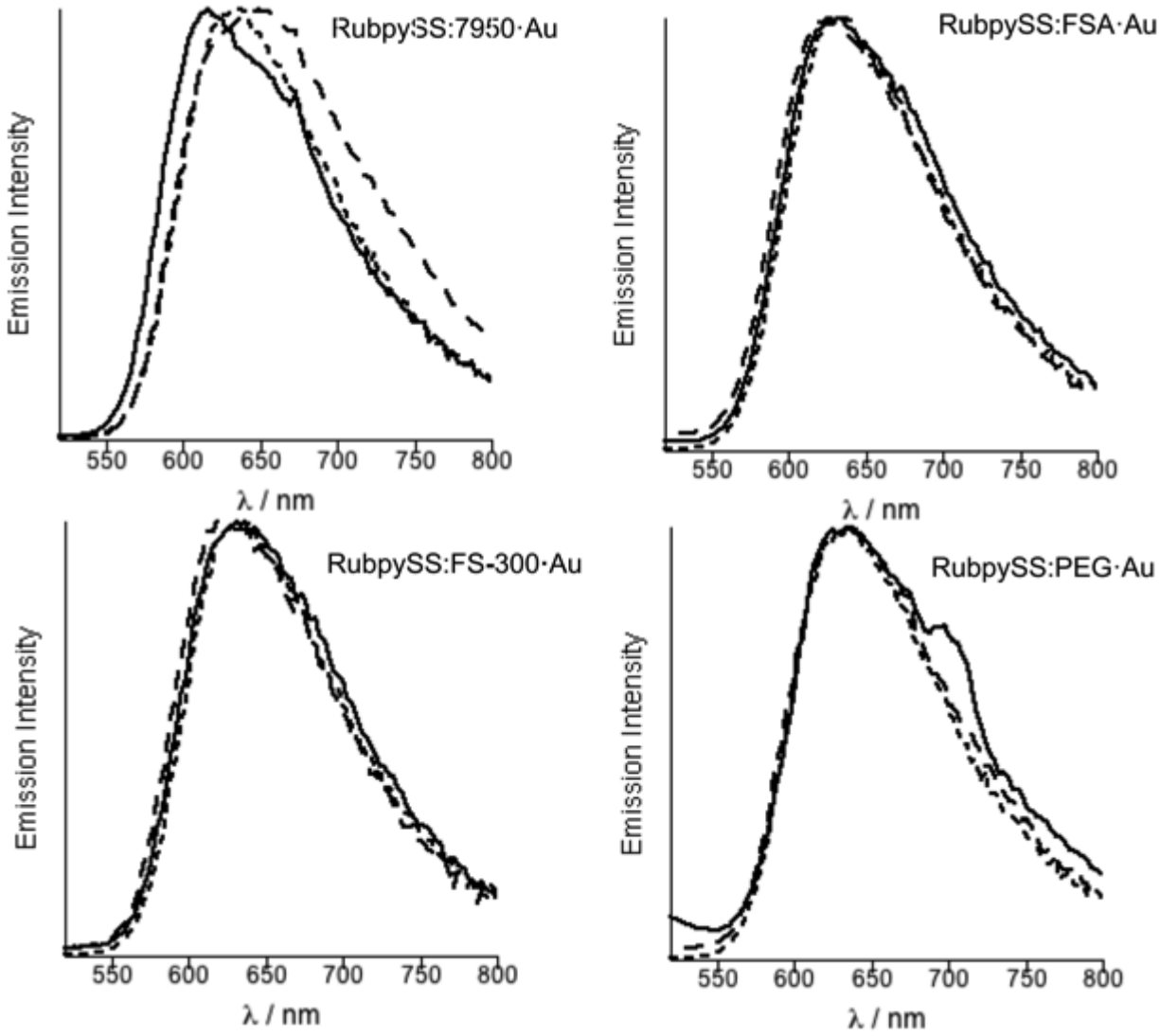

Figure 2. Steady state emission spectra of RubpySS without surfactant (short dash), co-coated with surfactant, before addition of BSA (solid) and after addition of BSA (long dash),. λ_{exc} = 465 nm, spectra corrected for instrument response. Spectral intensities are not to scale. BSA concentration is 16.5 µM. For simplicity of presentation Zonyl® 7950 is noted as 7950, Zonyl® FS-300 is noted as FS-300 and Zonyl® FSA as FSA.

Substrates were then further examined for changes upon the immersion of the substrates in a 16.5 µM solution of BSA in aerated water for 30 minutes, followed by washing with water. The luminescence data are summarised in Tables 1 and 2. Large 40 nm red shifts of the emission maxima of the surfaces of RubpySS and IrbpySS immersed with Zonyl® 7950 upon the addition of BSA were observed (Figure 2 and Figure 3). Upon the addition of BSA to the other co-coated

surfaces (Figure 2 and Figure 3), it was observed that the emission spectra exhibit small blue shifts, or do not shift at all, as is the case with RubpySS:PEG·Au and IrbpySS:FS-300·Au.

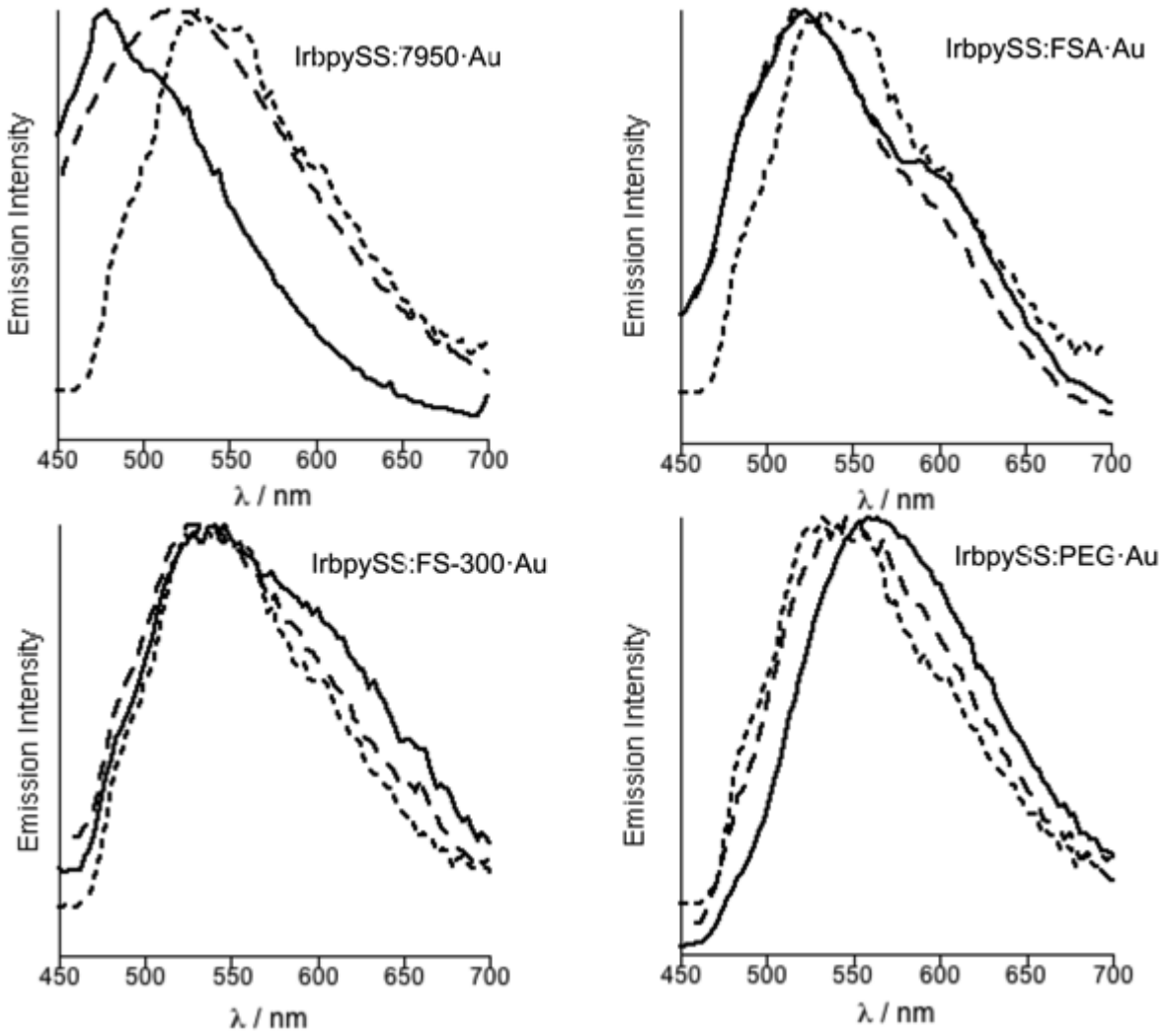

Figure 3. Steady state emission spectra of IrbpySS without surfactant (short dash), co-coated with surfactant, before addition of BSA (solid) and after addition of BSA (long dash). λ_{exc} = 360 nm, spectra corrected for instrument response (except for IrbpySS:FSA·Au). BSA concentration is 16.5 µM. Spectral intensities are not to scale. For simplicity of presentation Zonyl® 7950 is noted as 7950, Zonyl® FS-300 is noted as FS-300 and Zonyl® FSA as FSA.

Table 1. Photophysical properties of RubpySS·Au upon coating with surfactant. λ_{exc} = 445 or 465 nm. λ_{em} (τ) = 620 nm. The error in the measurement for λ_{em} is estimated to be ± 5 nm.

	λ_{em} / nm		τ / ns	
Surfactant used	without BSA	with BSA	without BSA	with BSA
None (RubpySS·Au)	630	640	210	283
Zonyl® 7950	610	650	115 (10%) 475 (90%)	214 (28%) 581 (72%)
Zonyl® FSA	635	630	165 (14%) 765 (86%)	31 (10%) 444 (90%)
Zonyl® FS-300	640	620	51 (7%) 440 (93%)	267
PEG	630	630	59 (5%) 546 (95%)	24 (6%) 475 (94%)

Table 2. Photophysical properties of IrbpySS·Au upon co-coatingwith surfactant. λ_{exc} = 330, 360 or 376 nm. λ_{em} (τ) = 480 or 520 nm. The error in the measurement for λ_{em} is estimated to be ± 5 nm.

	λ_{em} / nm		τ / ns	
Surfactant used	without BSA	with BSA	without BSA	with BSA
None (IrbpySS·Au)	532	550	12 (17%) 130 (83%)	15 (30%) 170 (70%)
Zonyl® 7950	480	520	7 (52%) 64 (48%)	133 (18%) 541 (82%)
Zonyl® FSA	530	530	31 (14%) 245 (86%)	67 (21%) 381 (79%)
Zonyl® FS-300	540	540	106 (23%) 462 (78%)	41 (13%) 310 (87%)
PEG	560	550	80 (11%) 428 (89%)	30 (16%) 351 (84%)

Luminescence lifetime measurements of the co-coated gold surfaces displayed a higher sensitivity of the local environment changes of the metal complex (Figure 4 and Tables 1, 2, Figure S1). All of the systems studied with the exception of IrbpySS:FSA·Au also revealed lifetimes on the surface longer than those of the complexes in aerated solution, further demonstrating the lack of quenching observed at the surface for these complexes.[6] The lifetimes of all of the complex:surfactant systems on gold substrates were longer than those without surfactant with the exception of

IrbpySS:7950·Au, which revealed a lifetime of 7 (52%), 64 (48%) ns compared with 12 (17%), 130 (83%) ns without a surfactant present. Notably the ruthenium complex RubpySS shows the largest effect of its luminescence lifetime in presence of the surfactants with lifetimes reaching to 475 ns (in the presence of Zonyl® 7950), 546 ns in the presence of PEG and 765 ns for the gold surface co-coated with Zonyl® FSA. We examined the effect of the surfactant alone in solution of the metal complexes in the presence and absence of oxygen. The luminescence lifetimes of RubpySS and IrbpySS were measured in 1:1 CH_3CN:H_2O upon addition of FSA, in the presence and absence of oxygen. FSA modified surfaces RubpySS:FSA·Au or IrbpySS:FSA·Au showed high enhancements of lifetimes in comparison with surfaces without any surfactant (Tables 1 and 2). The lifetimes in 1:1 CH_3CN:H_2O solution are much shorter than the surface 344 ns for RubpySS and 150 ns for IrbpySS. In the presence of excess FSA there is only a small increase in solution 20 % for and 15 % for RubpySS and IrbpySS, respectively. Deaerated solutions of RubpySS and IrbpySS have longer lifetimes 1046 and 280 ns which are not affected by the addition of surfactant. The studies show that the longer lifetimes observed in the surfaces are not simply an effect of surfactant presence but a result of the contribution of several factors. The first of these is the interaction of the surfactant molecules with the metal complex, which may partially protect the metal complex from oxygen quenching and change the polarity of the local environment. This in turn will affect the sensitive charge transfer luminescence signal of the complex. Secondly, the presence of surfactant may affect the alignment of the metal complexes on the gold surface thereby affecting luminescence luminescence quenching pathways by radiationless deactivation mechanisms from the gold surface.

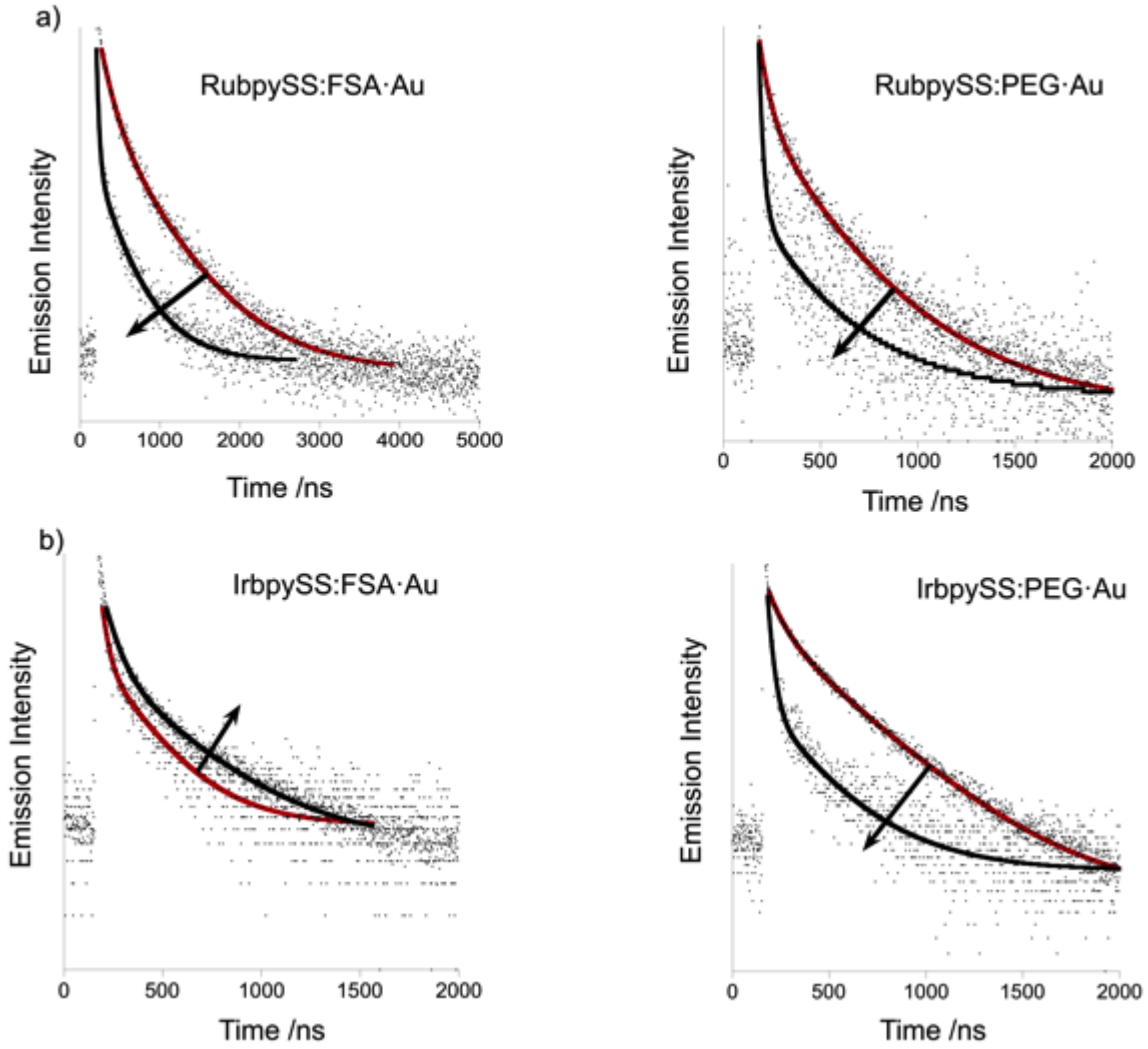

Figure 4. Representative luminescence lifetime decays with fitted lines of modified Au surfaces: (a) RubpySS surfaces before and after BSA addition**,** λ_{exc} = 465 nm λ_{em} = 620 nm; (b) IrbpySS surfaces before and after BSA addition λ_{exc} = 376 nm λ_{em} = 520 nm. . BSA concentration is 16.5 μM. The change after BSA addition is shown by the arrow.

We have previously studied the effect of BSA binding to RubpySS and IrbpySS in solution and on the gold surfaces.[6] The interaction in solution was attributed to electrostatic binding of the metal complexes with the protein and a stronger interaction of IrbpySS with a more hydrophobic BSA

pocket which led to changes of the BSA secondary structure. Surfactants are commonly used in treatment of biomolecules with surfaces and we examined the effect of BSA binding on the modified surfaces. Large increases in lifetimes for both complexes upon the addition of BSA for Zonyl® 7950 containing surfaces was observed with the lifetime of the IrbpySS:7950·Au being increased from 7 (52 %), 64 (48 %) ns to 133 (18 %) and 541 (82 %) ns , as well as an increase in lifetime for FSA with lifetimes of IrbpySS:FSA·Au surfaces increased to 381 ns. Both surfactants contain perfluorinated methylene groups and the results show that the presence of the surfactant still allows BSA binding which leads to an increases of the lifetimes of the iridium signal. However, a significant decrease in luminescence lifetime was observed for RubpySS:FSA·Au with the major component (86 %) of the lifetime falling from 765 ns to 444 ns upon the addition of BSA, which is still longer than the surface without any surfactant or BSA but the lifetime drop indicates change of the local environment of the metal complex which may be due to some surfactant displacement upon addition of BSA. When ethylene glycol ether groups were present in the surfactant, we observed a decrease in the luminescence lifetime of the complexes upon the addition of BSA, as evidenced by both the Zonyl® FS-300 and PEG mixed monolayer systems. In particular, Zonyl® FS-300 contains both perfluorinated methyl groups and ethylene glycol ether groups in its structure suggesting that these ethylene glycol groups may affect the luminescence lifetimes of the complexes more than the fluorinated groups in the studied systems. The results show that the presence of surfactant still allows monitoring of the BSA binding by luminescence lifetime and the polarity of the surfactant influences the relevant binding and changes of the luminescence lifetime.

Given the enhanced luminescence properties of the RubpySS and IrbpySS, complexes in the presence of a surfactant, we sought to determine whether this approach could be used to observe osmium(II) luminescence on a gold substrate. Osmium bipyridyl complexes are known to have low quantum yields of luminescence and it is particularly challenging to observe the luminescence of osmium complexes on gold surfaces. We had previously developed, OsbpySS,[6] an osmium(II) centred analogue of RubpySS, however on gold surfaces we could not observe measurable

luminescence. We created a mixed monolayer system with Zonyl® 7950 as the surfactant described above. Interestingly, we observed weak but characteristic ^{3}MLCT OsbpySS luminescence at the surface when co-coating with the Zonyl® 7950 took place, centred at *ca*. 740 nm (Figure 5). It was noted that the intensity of the spectrum above 760 nm is artificially high as a result of overcorrection due to low PMT sensitivity in this range. The lifetime of the emission was determined to be 38 ns, which is longer than the lifetime of OsbpySS in aerated solution (20 ns).[6]

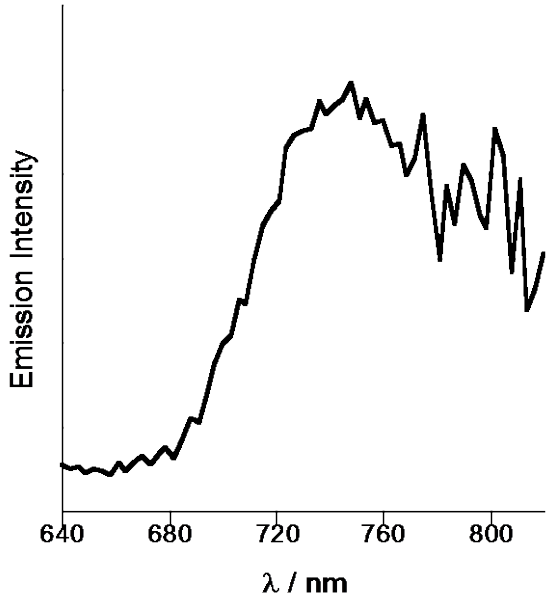

Figure 5. Steady state emission spectrum of OsbpySS:Zonyl® 7950·Au. λ_{exc} = 480 nm. Spectrum corrected for instrument response.

The studies show that the surfactant plays a role to enhancing the luminescence of the osmium complex, which is attributed to protection of oxygen and reduction of any deactivating processes from the surface.[3]

Surface Plasmon Resonance Studies

It was previously shown that BSA has stronger affinity for the metal-coated surfaces RubpySS·Au and IrbpySS·Au rather than plain gold, attributed to interaction of the metal complex with BSA, demonstrated by circular dichroism studies (Figure S2).[6] In order to examine the interaction of biological media with the mixed monolayer systems formed with surfactant and metal complex,

SPR spectroscopy was employed to indicate the recognition of the substrates by both BSA, and fetal bovine serum, a proteinous mixture extracted from bovine blood. FBS was chosen because of its common use in *in vitro* cell studies as a cell medium.[12]. The gold substrates with surfactant and metal complex were formed as indicated in the previous section, before equilibrating the substrates by flowing water over them at 50 µL min^{-1}, followed by injecting the protein across the surface at 1500 µL min^{-1} for 10 seconds. The flow rate was then reduced to 10 µL min^{-1} to allow recognition to occur, before 2 minutes of washing at 1500 µL min^{-1} and a further 10 minutes at 50 µL min^{-1}. The results are shown in Figure 6 for RubpySS systems and Figure 7 for IrbpySS systems.

The results show that for all mixed monolayer systems, injection of either BSA or FBS results in a large increase in response (ΔΘ) from the surfaces, indicating that both BSA and FBS do indeed bind to the mixed monolayer surfaces. In particular, it was observed for all surfaces with the exception of RubpySS:FS-300·Au (Figure 6c), that after washing of the surfaces, the response for BSA is decreased when compared with the same system without co-coating with surfactant. (Figure 6 and Figure 7). In the case of RubpySS:FS-300·Au (Figure 6c) we observed that the response is the same (0.42º), subsequent to the washing step. Interestingly, the response of FBS when injected across the mixed monolayer systems was lower than that of BSA, with the exception of substrates where Zonyl® 7950 was used as the surfactant. We postulate that the increased hydrophobicity of the surfactant compared with the other surfactants may induce binding with a more hydrophobic component of FBS, causing the increase in response compared with that of BSA. The presence of surfactant in the metal complex monolayer influences the binding of BSA and FBS in comparison with the monolayers of the respective metal complexes without the surfactant. The change in binding of the protein is affected by the change of surface hydrophobicity due to the presence of the surfactant and the relevant exposure of the metal complex which affects the binding affinity of the protein to the metal complex.

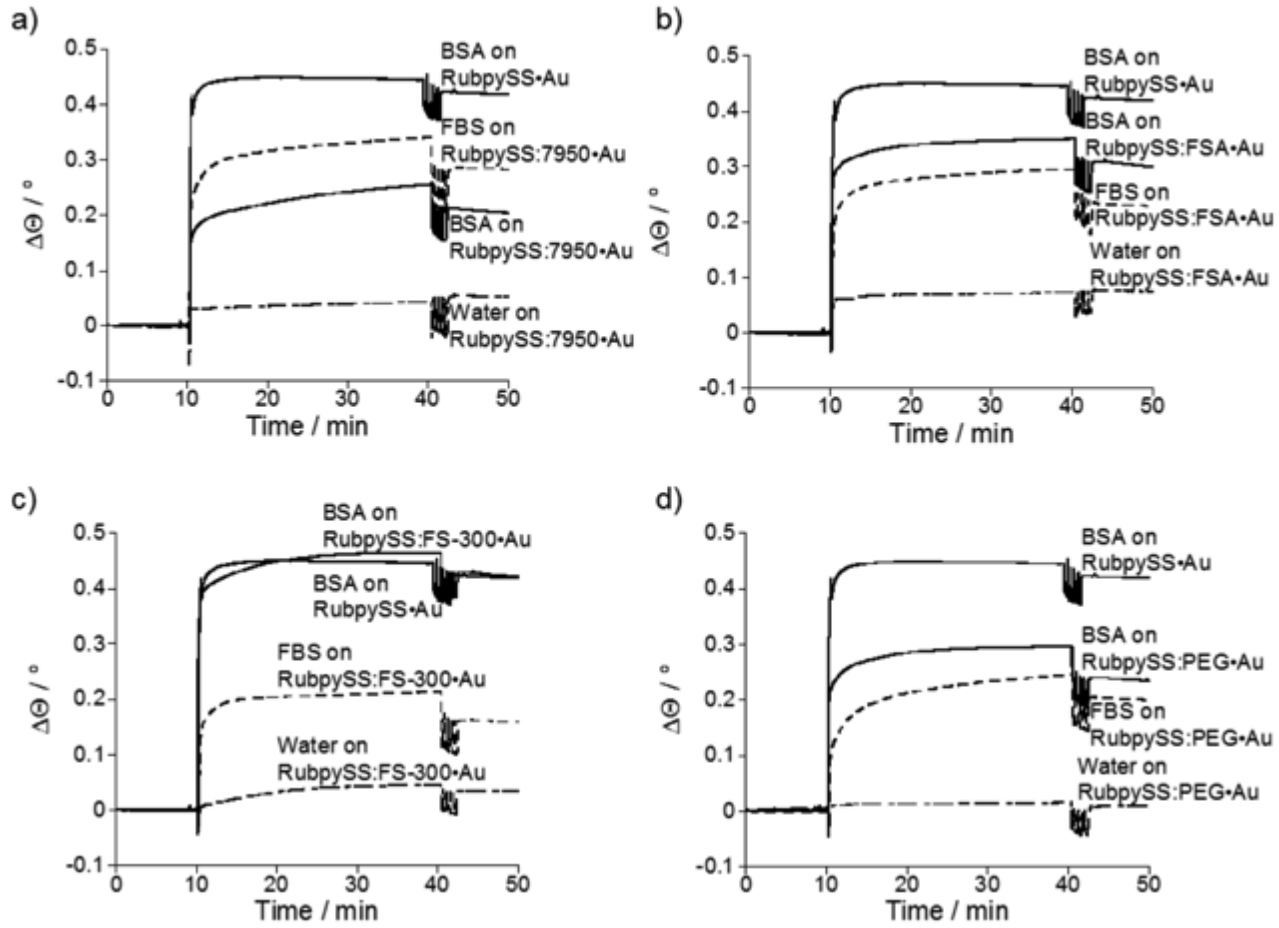

Figure 6. SPR sensorgrams of RubpySS and surfactant mixed monolayers. Surfactants used in each graph are Zonyl® 7950 (a), Zonyl® FSA (b), Zonyl® FS-300 (c) and PEG (d).

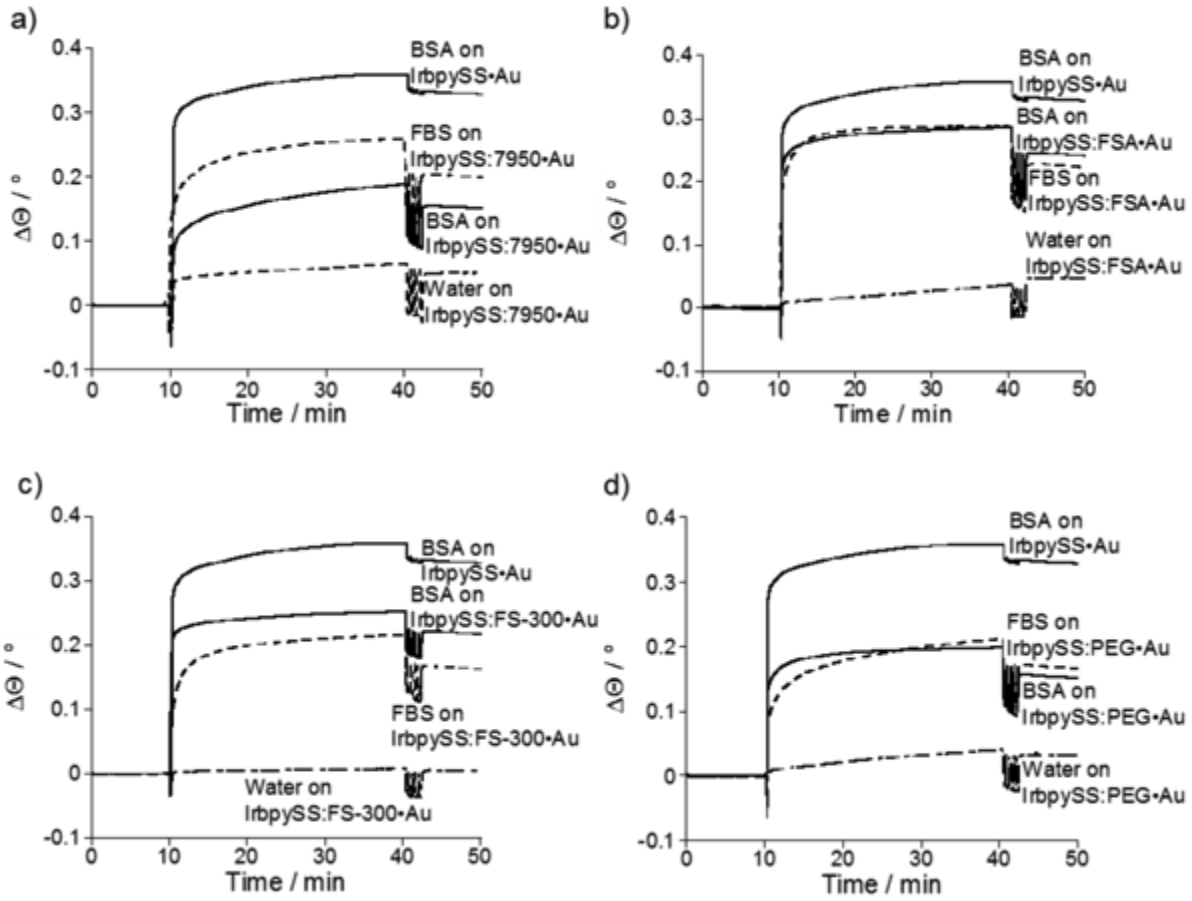

Figure 7. SPR sensorgrams of IrbpySSand surfactant mixed monolayers. Surfactants used in each graph are Zonyl® 7950 (a), Zonyl® FSA (b), Zonyl® FS-300 (c) and PEG (d).

X-ray Photoelectron Spectroscopy and Atomic Force Microscopy

To further demonstrate the effect of the BSA on the mixed monolayer system we examined the RubpySS:FSA and IrbpySS:FSA surfaces by X-ray photoelectron spectroscopy (XPS) and Atomic Force Microscopy (AFM) (Figures S3, S4, S5 and S6). The FSA surfactant has the hydrophobic fluorinated chains which influence the binding of the protein mixture. XPS elemental analysis of the RubpySS:FSA and IrbpySS:FSA before and after BSA show clearly the presence of fluorine environment, the presence of the Ru and Ir metals as well as the presence of BSA is indicated by a five fold increase of the N content. It is noticeable that the metal content does not change upon addition of BSA. The results clearly show that the monolayers still contain the fluorosurfactant upon BSA treatment, but there is an attenuation of the fluorine signal in both RubpySS:FSA and IrbpySS:FSA surfaces upon addition of BSA. The attenuation of the fluorine signal in comparison with the metal indicates for RubpySS:FSA is twofold whereas for IrbpySS:FSA is fivefold. This maybe contributed to the higher affinity of the iridium complex for BSA, previously indicated by circular dichroism which leads to some displacement of the fluorinated surfactant or it may be attributed to the different alignment of the metal complex with the surfactant which influences the BSA binding. AFM studies of the surfaces without surfactant, with surfactant and with BSA show a clear change of the morphology upon surfactant interaction (Figure S7). Addition of BSA shows a coverage of the gold surface with the BSA which is expected as BSA can cover all areas and interact with either the metal complex, free gold sites or metal complex and surfactant. The roughness of both types of surface decreased on BSA addition (RubpySS:FSA R_q = 2.18 nm; RubpySS:FSA+BSA R_q = 1.13 nm and IrbpySS:FSA R_q = 1.67 nm; IrbpySS:FSA+BSA R_q = 0.92 nm) indicating an overall smoothing of the surface due to uniform coating of BSA.

Conclusions

We have shown that fluorinated surfactants enhance the luminescence properties of ruthenium and iridium metal complexes on gold surfaces leading to longer luminescence lifetimes and in the case of osmium complexes, the co-coated surfaces display osmium luminescence, not previously observed on surfaces without a surfactant. The surfaces co-coated with surfactants are responsive to binding of albumins, providing the potential of developing devices for monitoring recognition events on surfaces based on luminescence lifetime measurements and changes in SPR signal. It was observed that the luminescence lifetime of the complexes in the presence of BSA was enhanced when co-coated with hydrophobic surfactants, and quenched in the presence of more hydrophilic surfactants. In all cases but one the lifetimes were longer than the plain metal complex on surfaces, demonstrating that the surfactant may be protecting the metal complex from quenching mechanisms induced by the gold surface. Upon interaction with BSA, the luminescence lifetimes drop slightly from the values of the surfaces with only surfactant but they are still longer than the surfaces coated with plain metal complexes with one exception of the RubpySS with FS300, confirming the change in the environment around the metal complex due to the interaction of BSA and surfactant. Through SPR spectroscopy, we showed that in general BSA adsorption is decreased when the surfaces are co-functionalised; with the exception of RubpySS:Zonyl® FS-300; which agrees with the luminescence lifetime results. The results with FBS treated surfaces indicate that surfaces co-coated with Zonyl® 7950 are most susceptible to biomolecular recognition in FBS, while less so in BSA. The results illustrate that metal complex surfaces co-coated with surfactants can be employed for monitoring biomolecular recognition. The choice of surfactant is important for the biomolecular binding but also for the influence of the luminescence properties of the metal complex and hence the signal response of the surface.

Supporting Information. This includes the experimental section and additional figures labelled as Figures S1-S7, which include XPS and AFM analysis and details of surface coverage estimation.

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Keywords. Luminescence; transition metal chemistry; photophysics; surface

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TOC

Gold surfaces functionalised with fluorinated surfactants and surface-active transition metal complexes based on ruthenium, iridium or osmium bipyridyl motifs, display enhanced luminescence signal and longer luminescence lifetimes with respect to gold surfaces without the surfactant treatment. The hydrophilicity of surfactant is revealed to be important in this effect. The surfaces are responsive to the addition of serum albumin, which can be monitored by changes in luminescence lifetime or luminescence signal.